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PREPARATION OF ACROLEIN AND ACRYLIC ACID

[アクロレインおよびアクリル酸の製造法]

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SPECIFICATION

1. Title of the Invention

PREPARATION OF ACROLEIN AND ACRYLIC ACID

2. Claims

(1) With a method which makes gaseous phase oxidation of propane with acrolein and acrylic acid using a catalyst in an oxidized state which contains 1 kind or 2 or more kinds which have been selected from a group which is comprised of bismuth, molybdenum, vanadium, selium, niobium, tantalum, cobalt, chromium, iron, nickel, zirconium tellurium, silver, copper, and phosphorus, or a catalyst in a oxidized state which contains an element or one kind or 2 kinds or more which is selected from a group comprised of vanadyl pyrophosphate, selium, niobium, molybdenum, tellurium, tungsten, iron, copper and silver, a method of manufacturing acrolein and acrylic acid which maintains less the stoichiometric amount with respect to the propane, which was transferred by the reaction, of oxygen amount within the supply gas which contains propane, and with separation from the composition fluid of the catalyst which was in a reduced state generated by the reaction, and by reoxidizing the catalyst before making contact, once again, with the propane.

(2) A method according to Claim 1 wherein the supply gas which contains propane does not contain in reality oxygen.

3. Detailed Explanation of the Invention

(Industrial Field of Application)

This invention is related to a manufacturing method for acrolein and acrylic acid from propane on a multicomponent oxidized catalyst. Acrolein is an important compound as a manufacturing raw for methionine and the like or as a raw material for obtaining acrylic acid by further oxidation. The acrylic acid as an ester is used in great quantities for the manufacture of every kind of synthetic resin. Polyacrylic soda is used in every kind of application as water absorbing polymer.

(Prior Art)

The manufacture of acrolein and acrylic acid with propane as the raw material is industrially widely used, achieving an extremely high level of absorption. On the one hand, many methods which manufacture acrolein and acrylic acid have been tried by oxidizing, using free oxygen, low cost propane instead of propylene, but the absorption rate of the generated acrolein and acrylic acid does not achieve a level which endures under industrial operations.

For example, in the case where there is obtained acrylic acid by vacuum oxidation of propane in the presence of $TeO(VO)_2P_2O_7$ catalyst, it is reported that there resulted a selection rate 30-35% of the acrylic acid using a propane conversion rate of 30% [Chem. Commun., 786 (1986)]. That is, with one times through the catalyst layer, only 10% of the propane that entered the layer was converted to the specified substance, with a large quantity of CO_2 and CO were byproducts, and it was difficult to eliminate the reaction heat which was generated by CO_2 and CO.

It has been reported as results from [Chem. Lett., 531 (1989)] that the specified substance has been obtained with a propane transfer rate of 20% and a selection rate on the order of 60% by oxidizing propane using free oxygen in the presence of bismuth-molybdenum catalysts, but with mixing the propane and oxygen in specific mol amounts, there were problems in executing the reactions within explosive ranges.

(Problems that the Invention is to Solve)

The goal of this invention is to provide a manufacturing method fro acrolein and acrylic acid that is very effective by oxidizing propane uwing free oxygen (gas containing oxygen).

(Means of Solving the Problems)

The inventors obtained results from researching methods of manufacturing acrolein and acrylic acid by oxidizing propane using free oxygen by a method which makes gaseous phase oxidation of propane with acrolein and acrylic acid using a catalyst in an oxidized state which contains 1 kind or 2 or more kinds which have been selected from a group which is comprised of bismuth, molybdenum, vanadium, selium, niobium, tantalum, cobalt, chromium, iron, nickel, zirconium tellurium, silver, copper, and phosphorus, or a catalyst in a oxidized state which contains an element or one kind or 2 kinds or more which is selected from a group comprised of vanadyl pyrophosphate, selium, niobium, molybdenum, tellurium, tungsten, iron, copper and silver, a method of manufacturing acrolein and acrylic acid which maintains less the stoichiometric amount with respect to the propane, which was transferred by the reaction, of oxygen amount within the supply gas which contains propane, and with separation from the composition fluid of the catalyst which was in a reduced state generated by the reaction, and by reoxidizing the catalyst before making contact, once again, with the propane. Their favorable discoveries were obtained by making a supply gas which contains propane react in a state where there was substantially no oxygen, to arrive at the invention.

The catalysts of this invention are multicomponent catalysts which contain elements which are selected from the groups already mentioned for a molybdenum-bismuth series or multicomponent catalysts which have elements which are selected from the above-mentioned vanadyl

pyrophosphate. The cases when these catalysts are used in reaction operations are many times used with fluid beds or movable beds. Consequently, with goals of improving the mechanical strength of the catalyst and reducing and maintaining the friction damage (attrition rate), there are many cases where a granulated ancillary material such as silica or aluminum is added to the previously mentioned multicomponent.

The manufacturing method with the catalyst mixes in the same way to arrive at a specified ratio hydroxides, carbonates, nitrates, organic salts, chlorides or phosphates of metal elements which are the formation components of the previously mentioned catalysts, adds silica gel or alumina sol, drying as a slurry. The obtained fine sphere-shaped solids are subjected to heat and solve, giving a mixture oxygen substance catalyst for metals which was the goal.

When the catalyst contains vanadyl pyrophosphate, heat is added to V_2O_5 within an alcohol medium such as isobutynol, reducing it to V_2O_4. Add a salt of a specific metal to the precursor $(VO)_2H_4P_2O_9$ which was obtained by adding phosphoric acid to V_2O_4, and obtaining a slurry after mixing, and with drying by a baking method there is obtained the catalyst.

This invention is a method for obtaining acrolein and acrylic acid by oxidizing propane using a catalyst in oxidized form. The above-mentioned catalyst transitions to an oxidized state by heating within a vacuum at 250-600 °C.

The amount of oxygen within the supply gas which is supplied to the oxidized catalyst is controlled so that the amount is less than the necessary stoichiometric amount with respect to the total amount of the propane which is converted during the reaction. The catalyst which was reduced by the oxidation of the propane is separated from the product fluid and oxidation of the catalyst occurs by heating once again in a vacuum before catalyzing once again with propane. The stoichiometric amount of the necessary oxygen with respect to the total amount of the propane which was converted during the reaction is the necessary amount for converting the propane to the acrylic acid and is oxygen of 2 mols with respect to 1 mol of the converted propane. More desirably, the amount of oxygen within the supply gas is less than 20% of the stoichiometric amount, that is, it is less than 0.4 mols oxygen with respect to 1 mol of converted propane. In order to improve the selectivity towards acrolein and acrylic of propane, if the catalyst is not reduced excessively during the reaction, it is desirable that the supply gas not contain oxygen in substantial amounts. Not only must there not be substantial amounts of oxygen in the supply gas, but before once again catalyzing the catalyst that was oxidized (baked under vacuum), but by stripping the gaseous phase oxidation from the catalyst, it is possible to elevate the reaction's selectivity. The reaction operation of this kind performs within one reaction region oxidation of propane, and oxidizes the reduced catalyst in a separate regeneration region, and it is convenient to execute in a recirculating solid phase reaction vessel. This

method, normally, is established by a combination of the following processes.

(Process I) Catalyze the supply gas which contains propane of approximately 1 mol%-100 mol%, preferably approximately 5 mol %- 30 mol % and O_2 of 0-20 mol % and an inactive gas for the remainder, and in a reaction area there has been distributed particles with diameters 20-200 μm which represents the catalyst in an oxidized state, in the reaction area of the re-circulating reaction vessel, in a temperature environment of 350-650 °C. The retention period for the gas within the reaction area is 0.5-30 seconds, and the retention period for the catalyst in the reaction area is on the order of 5-10 seconds.

(Process II) Eliminate the overflow substances which were generated by Process I from the reaction area and separate the reduced catalyst from the overflow gas, and transfer the reduced catalyst to the regeneration area of the re-circulating solid phase reaction vessel, absorbing the obtained acrolein and acrylic acid from the overflow gas.

(Process III) Using the reduced catalyst and the gas containing oxygen (normally air), oxidize at a temperature of 250-600 °C in the regeneration area. The retention time for the catalyst within the regeneration area is 5 seconds-10minutes. In addition, the retention period for gas which contains oxygen used in many applications is in the range of approximately 2 seconds-30 seconds.

(Process IV) Recirculate in the reaction area the oxidized catalyst which was obtained in Process 3. The re-circulation solid phase reaction vessel is used with the same form as that well known in the petroleum field as a (TRANSPORTED BED) or (RISER).

The reaction vessel pressure for Processes I-IV, for many applications, is 1-13 ATM in the range of atmospheric pressure-20kg/cm^2 G. In addition, the reaction raw materials can be petroleum of 100% purity and may be propane and propylene or a mixture of these chemicals and steam.

(Embodiments)

Embodiment-1

Implement an experiment which oxidizes in acrolein propane by using the re-circulation solid phase reaction vessel illustrated in Fig.1. The used catalyst has fine spheres which are comprised of SiO_2 0.6 wt. part manufactured by active component 1 wt. part and silica sol from $Bi_{0.85}Mo_{0.45}V_{0.54}Ag_{0.015}$, with a particle distribution of 25-150 μm and average diameter 65 μm.

The oxidized reaction parts of the vessel are A, inner diameter, 1 inch, height 1.5 m, reoxidized part of the catalyst C has an inner diameter 4 inches, and height 60 cm, and inserted amount of the catalyst which is placed in A-C is 4kg.

The retention period for the reaction area A (propane 10%, nitrogen 90%) is approximately 5 sec, and the temperature of the catalyst layer is 500 °C. The regeneration area C is set at 450-500 °C and the retention period is 4 seconds for air insertion.

The conversion rate of propane is 80%, the selectivity of acrloein is 72%, and the selectivity of acrylic acid is 9%.

Embodiment-2

Using a catalyst made up of fine particles (average particle diameter 60 μm) is comprised of silica 25% and active components as a mixture in the ration 9:1 of vanadyl pyrophosphate and telluric oxide, make a reaction using a reaction method with the same reaction vessel as that used in Embodiment 1. The retention period for the reaction gas (propane 10%, nitrogen 88%, and oxygen 2%) of reaction area is approximately 4 sec, and the temperature of the catalyst is 440 °C. The temperature of the regeneration area is 380-400 °C, and the retention period for the air is 4 sec.

The conversion rate of the propane is 55%, the selectivity of the acrylic acid is 65%, and the selectivity of the acrolein is 7%.

[Effect of the Invention]

According to this invention, there is a reduction and maintenance of gaseous phase oxidation within the region area or with substantially no oxygen, it is possible to obtain acrolein and acrylic acid from propane at high conversion and selectivity rates by reaction performance which has been conventionally reported. Because the necessary oxygen for the

reaction is supplied by catalysts which are in an oxidized state, there is no risk of explosion. The target concentration and high value within the reaction vessel outlet gas is obtained.

4. Brief Explanation of the Drawings

Fig. 1 shows the formation of the recirculation reaction vessel which is comprised of the riser type reaction vessel part A, the gaseous solid separator B and the catalyst reoxidation vessel C for the fluid bed.

1 flow entry part of the propane

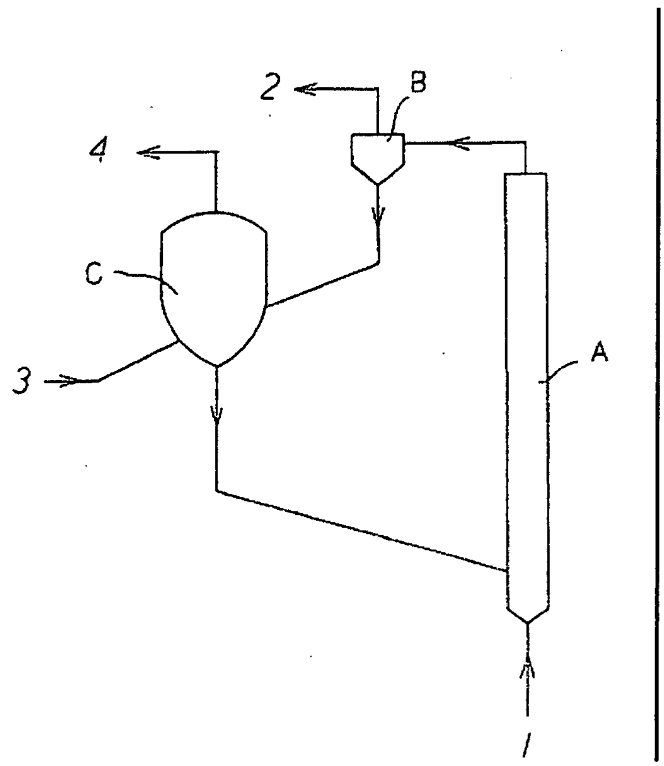
2 flow out part of the reaction generated substance

3 air flow in part used for reoxidation

4 exhaust gas outlet

Applicant Mitsui Toastsu Chemical

[Figure 1]



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